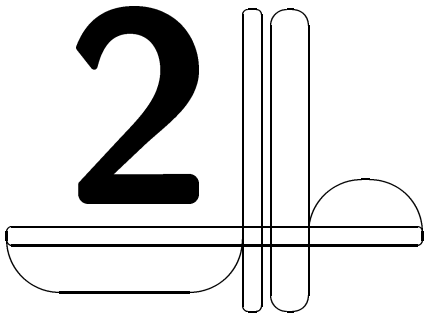

Screening of Coulomb potential in insulators

In this chapter we argue that screening of the Coulomb repulsion in non-polar insulators can to a large extend be determined from a point-dipole model. We apply these observations to C_{60}. The values found for the polarization energy and the effective on-site Coulomb interaction U compare well with experiment. For three dimensional systems the deviations from the Clausius-Mossotti result for the off-site screened Coulomb interaction are found to be small. In one and two dimensional systems, however, only local field effects contribute to the screening. At large distances the Coulomb interaction is unscreened and in 1D at intermediate distances the Coulomb interaction is even anti-screened.

2.1 Introduction

In model Hamiltonians such as the Hubbard Hamiltonian, the on-site Coulomb repulsion U, the energy it costs to put two electrons on the same lattice site relative to that on two different sites, is a very important parameter. In a system with on average one electron per atom, the ratio of U over the bandwidth W determines for instance whether the system is metallic or insulating and whether it is magnetically ordered or not [1]. In order to decide about the strength of correlations, precise knowledge of the on-site, and also the longer range, Coulomb interactions is crucial; the last view years, for instance, the relevance of Coulomb interactions has been an important topic in the debate on the High T_c superconductors, colossal magneto-resistance materials, Kondo- and heavy fermion systems, low dimensional organic salts and (doped) fullerenes and still there is no consensus about how correlated these systems actually are.

One of the most frequently used results from the theory of electric fields in solids is that an external potential $V(\mathbf{r},\omega)$ is screened inside a solid to a potential

Parts of this chapter are to be published by J. van den Brink and G. A. Sawatzky

$V(\mathbf{r},\omega)/\epsilon(\mathbf{r},\omega)$ due to the polarization field induced by the external potential. The calculation of the dielectric response function $\epsilon(\mathbf{r},\omega)$, or in momentum representation $\epsilon(\mathbf{q},\omega)$, is of the most fundamental importance because the dielectric response determines all electrical properties of the system. Full knowledge of macroscopic function $\epsilon(\mathbf{q},\omega)$ implies full knowledge of the electronic excitations of the total, interacting, system. In non-polar insulators the well-known result of Clausius and Mossotti [2] assumes that the static dielectric response function $\epsilon(\mathbf{r},0)$ reduces to a constant ϵ. The dielectric constant can then be expressed in terms of the polarizabilities of the ions present in the material.

In the table below the experimental value of U_{at} for some free transition metal ions and C_{60} in the gas phase and in some solids is shown [3–5]. Obviously U is greatly reduced in a solid.

One can attribute the reduction of U_{at} in the gas phase to U_{sol} in a solid to the polarization of all the other atoms in the solid if covalence effects, are neglected. In (ionic) insulators covalence effects are small, although for instance in transition metal oxides screening also occurs via the charge transfer from a ligand orbital to the $3d$ cation orbital or from a cation $4s$ orbital to a ligand orbital, which we do not consider here.

The question now is: can we use the dielectric response theory for non-polar insulators as a tool to calculate the effective Coulomb interaction in solids? Or, for instance: *is the effective value of the on-site Coulomb repulsion U_{sol} in insulating solids equal to U_{at}/ϵ?*.
The answer to the last question is: no, it is not. Below we discuss why this is the case.

On-site Coulomb Interaction U				
Ion	*config*	$U_{at}(eV)$	*Solid*	U_{sol} *(eV)*
Cu	d^9	16.3	CuS	7.0
Ni	d^8	18.0	NiO	7.5
			NiS	5.5
Co	d^7	16.2	CoS_2	4.2
Fe	d^6	14.7	FeO	7.0
Mn	d^5	20.2	MnO	7.0
C_{60}		3.4	C_{60}	1.6

In this chapter, we study the static dielectric response of a non-polar insulator to the Coulomb potential generated by two electrons that are placed in the system. It is shown that at large distances between two external potentials (electrons) the well known Clausius-Mossotti (C.-M.) theory of dielectrics is valid for three dimensional systems. However, at short distances between the electrons (typically a few lattice spacings) the Coulomb potential is a rapidly varying function of distance so that this theory has to be modified. These modifications are know in the literature as *local field corrections*, a quite inappropriate nomenclature because at very short distances

the C.-M. theory is simply incorrect and the local field terms dominate and are not small corrections. An underlying assumption in deriving the C.-M. relation is that the external potential can be considered as being uniform in a region around each atom, and that one can treat this region as a continuum. If the electrons are close to each other, one has to take into account that a lattice consists of a discrete set of atoms, whereas it is effectively treated as a continuum in the C.-M. theory.
In one or two dimensional systems (lines or planes of atoms) the screening of the (three dimensional) Coulomb field cannot be described by the C.-M. theory at all.

If the lattice is properly treated as a discrete set of atoms, it is possible to obtain the screening energy of the Coulomb interaction of two electrons on the same lattice point (the Hubbard U). Also the screened Coulomb potential at short distances and in one and two dimensional systems can be calculated.

2.1.1 Atomic polarizability

An atom in an electric field polarizes to screen the field. If an atom has, for instance, an occupied s-level and an empty p-level, the two levels mix in an electric field with an amount of $\int \phi_s(\mathbf{r})V(\mathbf{r})\phi_p(\mathbf{r})d^3\mathbf{r}$, and the two resulting wavefunctions are a linear combination of the p and s level, one with an energy lower than the original energy of the s level, and one with an energy larger than that of the original p level. This mixing of the p and s level leads to an asymmetric charge distribution, which represents the charge displacement that screens the potential $V(\mathbf{r})$. If we assume a linear response of the atoms to an electric field, the induced dipole moment $\mathbf{p}(\mathbf{r}_i)$ on an atom on site $\mathbf{r}_i$ is proportional to the local field $\mathbf{F}(\mathbf{r}_i)$:

$$\mathbf{p}(\mathbf{r}_i) = \alpha_i^{\mathrm{el}}\mathbf{F}(\mathbf{r}_i), \tag{2.1}$$

where α^{el} is the polarizability of an atom due to electrons that screen the external field. In a semiclassical approximation α^{el} is proportional to the volume of the ion under consideration. Assuming the electric field is constant over the size of the atom, the energy of the system is lowered due to the induced dipole moment by an amount of $\Delta E_i = -\frac{1}{2}\alpha_i^{\mathrm{el}}\ |\mathbf{F}(\mathbf{r}_i)|^2$.

In an ionic solid an external field also causes ions as a whole to move from their equilibrium positions in order to screen the field. The associated polarizability is the atomic displacement polarizability α^{dis}. The displacement polarization is related to the phonons.

2.1.2 The Clausius-Mossotti relation

The dielectric function of a macroscopic system is defined as the ratio of the displacement field $\mathbf{D}$ and the average electric field in the solid $\mathbf{E}$. These two fields are related through the polarization field $\mathbf{P}$ by $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$. All these fields are macroscopic fields and in order to relate the macroscopic quantity ϵ to the microscopic quantity α_i, the atomic polarizability, the local field $\mathbf{F}$ has to be introduced, being the field at

a lattice site. The *average* atomic polarizability α is introduced with: $\alpha = \frac{1}{v}\sum_i \alpha_i$ where α_i is the polarizability of atom i, and v is the volume occupied by the atoms under summation. If the lattice is thought of as a lattice of induced point-dipoles, the dipole moment of each dipole is proportional to the local field: $\mathbf{P} = \alpha\mathbf{F}$. If we imagine that the dipole is placed in a spherical cavity in the polarized dielectric, the local field in the center of the cavity is $\mathbf{F} = \mathbf{E} + 4\pi\mathbf{P}/3$. It is assumed that the field in the cavity is constant, which need not necessarily be the case for spatially rapidly varying fields. The approximation that the atoms, which we removed to create the cavity, do not contribute to the electric field, can be proven to be exact if the crystal has inversion symmetry. When the previous equations are combined, one obtains

$$\epsilon = \frac{1 + 8\pi\alpha/3}{1 - 4\pi\alpha/3}, \quad \text{or} \quad \frac{\epsilon - 1}{\epsilon + 2} = 4\pi\alpha/3, \tag{2.2}$$

which is the well know Clausius-Mossotti relation. This relation holds for point-dipoles on a lattice that has point inversion symmetry.

The question arises as to which atomic polarizability should be used in an ionic solid: α^{el} or α^{dis}? This depends on the frequency of the external field. If the frequency is low the ions can follow the field and are displaced in phase with the external field and the dielectric constant to be used is ϵ_0 which is determined by the sum of α^{el} and α^{dis}. If there is a phase difference between the displacement and the applied field, the response of the system can be described in terms of a complex dielectric function. If on the other hand the frequency is high, much higher than the typical phonon (Debye) frequency ω_{D}, the field cannot couple to the phonons anymore and the dielectric constant to be used is ϵ_∞ which is determined by α^{el} only.

Note that ϵ_∞, although frequently used in literature, is not a very precisely defined quantity. Certainly $\epsilon_\infty \neq \epsilon(\omega \to \infty)$ as $\epsilon(\omega \to \infty)$ is exactly unity, because in the limit that the frequency is very large, even the electrons cannot respond to the applied field. So in fact the best way to define ϵ_∞ is as the dielectric response function due to the electrons only. The C.-M. relation for high frequencies is also know as the Lorentz-Lorenz relation. The refractive index n of the system, is closely related to the dielectric response function: $\epsilon = n^2$.

2.2 Screening of the Coulomb potential

Let us look how the Coulomb potential between electrons in a solid is modified by the induced polarization of the atoms. Usually it is assumed that the dielectric constant obtained by the Clausius-Mossotti relation can be used to account for these screening effects. We show below that this is not right if the distance between the electrons is of the order of the lattice spacing.

It is advantageous to develop a simplified picture before going into the mathematical formulations. In figure 2.1 the potential around two charges is drawn schematically. The dotted line represents the reduced, screened Coulomb potential due to one single charge. The unscreened on-site Coulomb repulsion U_0 is the energy it costs to move the two charges to the same site. Expressed in the electron affinity E_A and

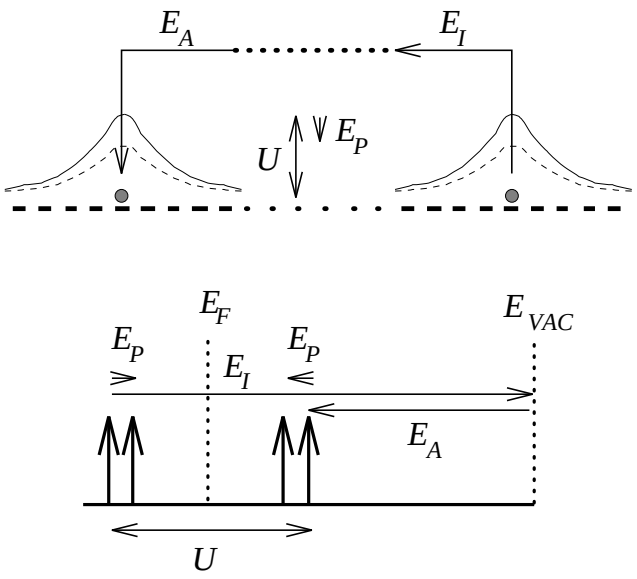

Figure 2.1: Schematic representation the effect of screening. The two filled circles represent electrons. In the upper curve the ionization energy, electron affinity and the (screened) Coulomb potential are shown. In the lower figure an energy scheme of this system is shown from which it is clear that $U_{eff} = U_0 - 2E_p$.

ionization potential E_I of the system: $U_0 = E_I - E_A$. If we now introduce screening, moving the first charge towards the second can be thought of as building up a test charge in the screened potential of the first charge and destructing the second charge in its own screened potential. This reduces E_I by the polarization energy E_p and enhances E_A by E_p, leading to a screened (effective) on-site Coulomb repulsion

$$U_{eff} = E_I - E_A - 2Ep. \tag{2.3}$$

The mathematical description of the microscopic response of a system of point-dipoles to external fields was developed by Mott and Littleton [6] and has proven to be a powerful method to calculate for instance local field corrections for point-charge defects [7] and (surface) core-level shifts in photoemission [8–10].

Consider two electrons, one at the origin of our coordinate system and one at $\mathbf{R}$. The aim is to calculate the electrostatic energy V of the system as a function of $\mathbf{R}$. The total energy consists of four parts: the potential energy due to the monopole-monopole, monopole-dipole and dipole-dipole interactions plus the energy stored in the induced dipoles [7]. The total electrostatic energy is given by:

$$V(\mathbf{R}) = \frac{e^2}{R} - \frac{1}{2}\sum_i \mathbf{d}_i \cdot \mathbf{p}_i \equiv \frac{e^2}{R} - 2E_p(\mathbf{R}), \tag{2.4}$$

where $\mathbf{d}_i$ is the total external monopole field and $\mathbf{p}_i$ the induced dipole moment at site i. The bare Coulomb repulsion is reduced by the polarization energy $2E_p(\mathbf{R})$, as defined in the last part of equation (2.4). Now the dipole moment at each site

has to be determined. According to equation (2.1) the induced dipole moment is proportional to the local field on the atom, leading to:

$$\begin{aligned} \mathbf{p}(\mathbf{r}) &= \alpha e^2 \mathbf{r}/|r|^3 + \alpha e^2(\mathbf{r}-\mathbf{R})/|r-R|^3 \\ &+ \alpha \sum_{\mathbf{l},\mathbf{l}\neq 0} \frac{1}{|l|^5} \{ [3\mathbf{p}(\mathbf{r}+\mathbf{l})\cdot\mathbf{l}]\,\mathbf{l} - |l|^2 \mathbf{p}(\mathbf{r}+\mathbf{l})\}. \end{aligned} \tag{2.5}$$

This equality for N atoms results in DN coupled equations for $\mathbf{p}(\mathbf{r}_i)$, where D is the dimensionality of the system. If the symmetries of the problem are taken into account, the number of equations that actually have to be solved can be substantially reduced. The matrix representation of equation (2.5) in Cartesian coordinates is:

$$p_i^\mu = \alpha_i d_i^\mu + \sum_\gamma \sum_{j,j\neq i} M_{ij}^{\mu\gamma} p_j^\gamma, \text{ with } \mu,\gamma = x,y,z. \tag{2.6}$$

The elements of the matrix that represents the dipole-dipole interactions are given by:

$$M_{ij}^{\mu\gamma} p_j^\gamma = \alpha_j (3 l_{ij}^\mu \; l_{ij}^\gamma \; |l_{ij}|^{-5} - |l_{ij}|^{-3} \; \delta_{\mu\gamma}), \tag{2.7}$$

where $\mathbf{l}_{ij} = \mathbf{l}_i - \mathbf{l}_j$ is the vector connecting the two dipoles. The solution of this set of equations gives the exact effective potential for the electrons. In some cases the equation can be solved in wave-vector space [11], but in general the less cumbersome method is to solve the equation numerically in real space.

2.2.1 Continuum limit

If the summations in equation (2.4) and (2.5) are replaced by integrations the continuum limit of the screened Coulomb potential is obtained. From the C.-M. relation follows that

$$\mathbf{p}_i = \alpha_i \mathbf{F}(\mathbf{r}_i) = \alpha_i \frac{\epsilon+2}{3\epsilon} \mathbf{d}_i \tag{2.8}$$

Using this result in equation (2.4) for a mono-atomic solid and realizing that

$$\int d^3\mathbf{r} \frac{\mathbf{r}\cdot(\mathbf{r}-\mathbf{R})}{r^3|r-R|^3} = 4\pi/|R|, \tag{2.9}$$

the well know result

$$V(\mathbf{R}) = \frac{e^2}{\epsilon R} \tag{2.10}$$

is obtained. This shows that the method described above to find the screened Coulomb potential generates the C.-M. result if the lattice is treated as a continuum.

2.2.2 Partial continuum limit

Suppose that the dipole-dipole field is slowly varying in space, which is reasonable if the distance between the atoms is fairly large, as the dipole-dipole interactions fall off as one over the distance cubed. In that case the result of equation (2.8) can be used and inserted in equation (2.4):

$$\begin{aligned} 2E^p(\mathbf{R}) &= -\frac{1}{2}\alpha\frac{\epsilon+2}{3\epsilon}\sum_{\mathbf{r},\mathbf{r}\neq 0,\mathbf{r}\neq\mathbf{R}}\{\mathbf{r}/|r|^3+(\mathbf{r}-\mathbf{R})/|r-R|^3\}^2 \\ &= -\frac{1}{2}\alpha\frac{\epsilon+2}{3\epsilon}\sum_{\mathbf{r},\mathbf{r}\neq 0,\mathbf{r}\neq\mathbf{R}} 1/|r|^4+1/|r-R|^4 \\ &+ 2(\mathbf{r}\cdot(\mathbf{r}-\mathbf{R})/(r^3|r-R|^3) \\ &= -\alpha\frac{\epsilon+2}{3\epsilon}L(\mathbf{R}). \end{aligned} \tag{2.11}$$

The first two terms on the second line in the sum above are constants which are just an offset for the potential, so we are only left to determine the lattice sum $L(\mathbf{R})$. The lattice sum for a simple cubic lattice with lattice parameter a is evaluated, by performing an exact sum inside a sphere of radius $300a$, and using the continuum result outside the sphere. The sum converges well and the result for $L(\mathbf{R})$ and $R\,L(\mathbf{R})$ is shown in figure 2.2. For large distances between the electrons ($R > 3-4a$) the continuum approximation is very good, i.e. if $R\to\infty$ then $\mathbf{R}\,L(\mathbf{R})\to 4\pi a$. At short distances, however, there is considerable difference between the continuum limit and the lattice sum. Most strikingly for $R=0$ the continuum result diverges, but the lattice sum is $L(0)=16.53$. The repulsive potential at short distances fluctuates around $1/\epsilon|R|$ and depends not only on the distance R, but also on the direction of $\mathbf{R}$ with respect to the lattice.

From the calculation above we can easily relate U_{at} and U_{sol}:

$$\begin{aligned} U_{sol} &= U_{at}-\sum_i \alpha_i L^i(0)\frac{\epsilon+2}{3\epsilon}\frac{14.4}{4\pi a_i}\ \text{eV} \\ &= U_{at}-\frac{14.4\ L(0)}{4\pi a}(1-\frac{1}{\epsilon})\ \text{eV} \end{aligned} \tag{2.12}$$

where a is distance between nearest neighbor atoms in Å. The summation in the first equation is the sum over different sublattices. The last equation holds for a mono-atomic crystal. In the table below the lattice sums $L(0)$ for different crystal structures are given (see also [12]). The bi-atomic rock salt structure consists of two FCC sub-lattices A and B shifted half a lattice spacing with respect to each other. The lattice sum for the rocksalt structure in the table below is the outcome of summation (2.11) starting at a lattice point of sub-lattice A and summing over all points of sub-lattice B.

A point to be addressed now is what dielectric constant should be used in the equations above. This depends on the bandwidth of the charges in the system. If

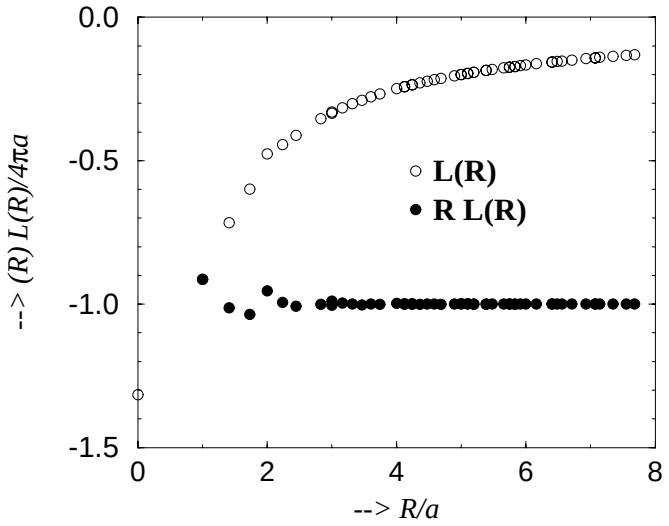

Figure 2.2: Lattice sum $L(R)$ and $RL(R)$ as a function of distance in a 3 dimensional cubic system.

the charges are completely localized, the system can fully relax and also the phonons contribute to the relaxation energy so that the appropriate dielectric constant is ϵ_0. If the charges have a finite bandwidth, however, the charge is dynamically screened and the dielectric constant to be used is $\epsilon(\omega)$, where ω is in the order of the bandwidth.

Lattice sums for on-site Coulomb repulsion	
Crystal structure	$L(0)$
Simple Cubic	16.53
BCC	22.64
FCC	25.34
Rock salt	10.20

Screening of Charge Transfer Energy

The charge transfer energy Δ is the energy associated with the transfer of a charge from one sub-lattice to another. In an uncorrelated ionic insulator the Madelung potential V_{M} determines this energy,

$$\Delta = V_{\mathrm{M}}(A) - V_{\mathrm{M}}(B), \tag{2.13}$$

where A and B denote to lattice sites on different sublattices.

The Madelung potential is the potential at a lattice site due to all other charges in the system:

$$V_{\mathrm{M}}(i) = \sum_{j,j\neq i} \frac{q_j}{|\mathbf{R}_{ij}|} \tag{2.14}$$

Is the Madelung potential screened?
It is tempting indeed to argue that the effective Coulomb potential is the bare one divided by ϵ and therefor the effective Madelung potential is $V_{\mathrm{M}}(i)/\epsilon$ so that the charge transfer energy is screened substantially.
The electric field in the groundstate at a site i is given by

$$\mathbf{d}_i^0 = \sum_{j,j\neq i} q_j \frac{\mathbf{R}_{ij}}{|\mathbf{R}_{ij}|^3}. \tag{2.15}$$

In order to calculate the charge transfer energy one has to evaluate the energy associated with the process of removing a charge from an atom in a particular sub-lattice and putting it on an atom far away in a different sub-lattice. The electric field in the system with one extra charge at site k it is

$$\mathbf{d}_i = \mathbf{d}_i^0 + q_k \frac{\mathbf{R}_{ik}}{|\mathbf{R}_{ik}|^3}. \tag{2.16}$$

If the lattice has inversion symmetry it is trivial to prove that in the groundstate there is no electric field *at any site*: $\mathbf{d}_i^0 = 0$. No field means no induced dipole moment so that the groundstate energy is not affected by atomic polarizabilities. There is a net electric field in the system with one extra charge, but this field is fully due to the one extra charge so that the polarization energy can be calculated using equations (2.4-2.7) without reservation, leading to

$$\Delta_{eff} = V_{\mathrm{M}}(A) - V_{\mathrm{M}}(B) - Ep(A) - Ep(B) \tag{2.17}$$

This implies that the effective Madelung potential is equal to the bare one if the system is inversion symmetric. The charge transfer energy is screened in a way that is similar to the on-site Coulomb repulsion. This, again, is a result that can only be obtained if the lattice is treated as a discrete set of atoms and not as a continuum.

NiO and C_{60}

Let's apply this result to two real systems, NiO and C_{60}.

- The lattice parameter in FCC ordered C_{60} is 14.1 Å, its dielectric constant $\epsilon = 4.4$ [13] and according to the C.-M. relation $\alpha_{C_{60}} = 89.8$ Å^3. This leads to $2E_p = 1.6$ eV, in remarkable agreement with the experimental value of $2E_p = 1.7 \pm 0.2$ eV and the result $2E_p = 1.7$ eV that can be derived from the surface core level shift calculations in [10], where dipole-dipole interactions are taken into account exactly.

- NiO has a rock-salt structure. Covalence effects in NiO are surely present, from bandstructure calculations it is known that the ligand p - cation $4s,p$ hybridization is considerable, giving rise to a notable amount of cation $4s,p$ character in the groundstate [14,15]. Neglecting these, it is found from $a = 2.06$ Å , $\alpha_{Ni^{2+}} = 0.89$ Å^3 [16] and $\epsilon = 5.2$ [17] that $\alpha_{O^{2-}} = 1.55$ Å^3. The free O^{2-} ion is not stable, but the value for the polarizability above is within the range $\alpha_{O^{2-}} = 0.5 - 3.2$ Å^3 found for different ionic crystals [18]. Using this value for the nickel and oxygen polarizability, we find from equation (2.12) for the nickel site $2E_p^{Ni} = 7.0$ eV, where the value derived from core-level photo-emission experiments is $2E_p = 10.5 \pm 0.5$ eV (neglecting covalence) and for the oxygen site we find $2E_p^{Ox} = 11.2$ eV. The effective charge transfer energy is $\Delta_{eff} = \Delta_0 - E_p^{Ni} - E_p^{Ox} \equiv \Delta_0 - E_p^{ct}$, where Δ_0 is the bare charge transfer energy, as for instance found from Madelung potential calculations. From this calculation we find that the screening of the charge transfer energy is $E_p^{ct} = 9.1$ eV.

From these examples it can be concluded that the partial continuum limit leads to very reasonable values of the polarization energy.

Screening of multipole Coulomb interactions

The Coulomb interaction in atoms causes besides the monopole interaction also higher order multipole contributions. These are surely not negligible and give rise to the rich multiplet structure encountered in atom(-like) excitation spectra.

The electric field generated by a charged atom depends mainly on the total charge of that atom, and therefor the response of the system to this field doesn't depend on the spin-state at hand. The monopole Coulomb repulsion is screened, but for instance the Hunds rule exchange coupling between intra-atomic electron spins is not. Higher order multipole Coulomb interactions are only weakly screened because of the short range of the multipole fields. This leads to the challenging conclusion that in the analysis of strongly correlated systems one has to take full account of the atomic multiplet structure.

Screening at surface

Within the partial continuum limit, where it is assumed that the dipole-dipole interaction can be treated at the Clausius-Mossotti level, the polarization energy only depends on the lattice sum $\mathrm{L}(\mathbf{R})$. If the charges are at the same lattice site then $L^{bulk}(0) = \sum_{i \in bulk} \frac{1}{r_i^4}$, where the sum is over all lattice points. It is easy to show that the lattice sum for two charges at the surface is equal to half the sum for the bulk plus half the sum for a free standing layer: $L^{surf}(0) = \frac{1}{2}L^{bulk}(0) + \frac{1}{2}L^{layer}(0)$, so that

$$E_p^{surf} = (E_p^{bulk} + E_p^{layer})/2. \tag{2.18}$$

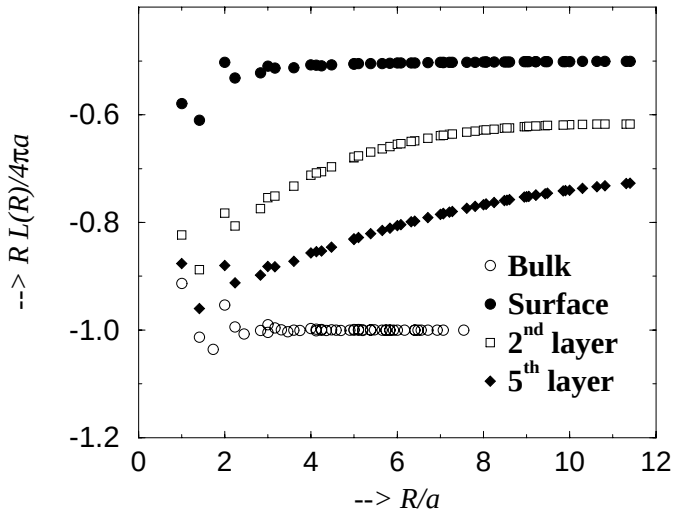

Figure 2.3: Lattice sum multiplied by distance as a function of distance going from surface to bulk in a cubic system.

The lattice sum for two charges in a plane parallel to the surface is shown in figure 2.3. From this figure we can conclude that if the distance between the charges is large, the polarization energy at the surface is exactly half the bulk value. This implies according to equation (2.18) that at large distances between the charges the polarization energy in the free standing layer doesn't play any role.

From this figure we also see that if the plane, parallel to the surface, where the electrons move in, is taken further away from the surface, the screening energy gradually goes from the surface value to the bulk value.

2.2.3 Exact results

Calculation method

If one wants to take the dipole-dipole interaction into account without using the Clausius-Mossotti relation, one has to solve the matrix equation (2.6).

Only a limited number of equations can be solved numerically, typically a few thousand. In principle N lattice points result in DN equations, where D is the dimension of the system, but by symmetry the number of equations can be reduced, sometimes even by an order of magnitude. To be confident about the convergence of the results we subdivide the lattice into four regions. For atoms within a sphere of radius r_0 around each electron a system of equations is set up. These two spheres are placed inside a larger sphere with radius r_1 for which the partial continuum result is used. The induced dipole field of the atoms in this sphere is added as an external field to the atoms inside the spheres with radius r_0. Outside the sphere with radius r_1 the continuum result is used.

To obtain a result that is accurate within 1%, as the results below, typically a r_0

of five lattice spacings and r_1 twice as large is sufficient.

Results for C_{60}

There are a number of experiments on C_{60} and mono-layers of it on different substrates from which the effective value of the on-site and nearest neighbor Coulomb interaction is extracted [5, 19–21]. These values can be compared to the result of the exact calculations.

The nearest neighbor distance in FCC ordered C_{60} is 10 Å, it's dielectric constant $\epsilon = 4.4$ [13] and according to the C.-M. relation $\alpha_{C_{60}} = 89.8$ Å^3. The atomic on-site Coulomb interaction for C_{60} is 3.4 eV [5]. In the table below the effective Coulomb repulsion on-site, U^{eff}, and between electrons on neighboring sites, V^{eff}, is given. Four different geometries are considered. First the bulk values are presented. In the following rows the theoretical values for a (111) surface of bulk C_{60}, a free standing hexagonal layer and a hexagonal monolayer on a metallic substrate are given. In the last calculation also the image charges and image dipoles that are induced in the metal and their interaction with the real charges and dipoles is taken into account.

Effective Coulomb interaction for C_{60}		
Geometry	U^{eff}	V^{eff}
Bulk theory	1.75	0.43
Bulk exp. [20]	1.7 ± 0.2	0.4 ± 0.2
(111) Surface	2.04	0.62
Free Layer	2.49	0.92
Monolayer on Metal	1.00	0.00

The effective Coulomb interaction obviously increases going from bulk to surface to free standing layer, because the number of nearest neighbours, that contain about half of the screening energy, decreases. A metal substrate screens the Coulomb interaction very efficiently. If a charge is present at a distance r from a grounded metallic surface, one can find the potential energy of the system by solving Poisson's equation with the boundary condition that the potential at the metal surface be zero. This boundary condition is also met if the metal is replaced by a charge of opposite sign at a distance $-r$ from the surface. This charge is called the image charge. Because the boundary conditions of both systems are the same the uniqueness of the solution of the Poisson's equation implies that the potential outside the metal surface is the same for both systems. So the problem of a charge in the presence of a grounded metal surface can be mapped on a problem of two charges without any extra boundary conditions. The same holds for dipoles. It turns out that a very large contribution to the screening comes from the interaction of the charges and their images. The screening energy, for instance, of an electron at 5 Å from a metal surface is about 0.7 eV. This explains why the Coulomb interaction in a monolayer of C_{60} on a metal substrate is so heavily screened.

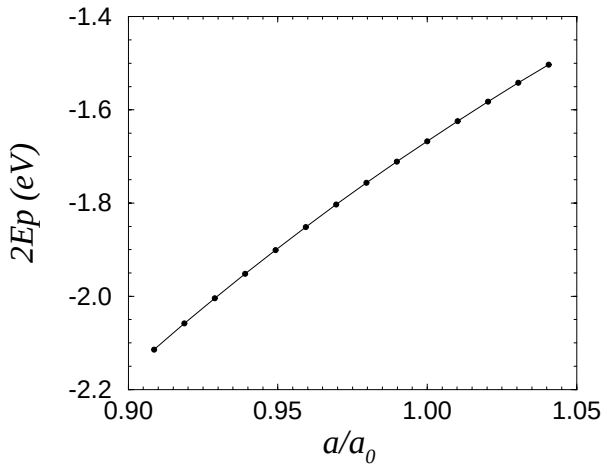

Figure 2.4: Dependence of the polarization energy on lattice parameter a in an FCC lattice of C_{60} molecules. The nearest neighbor distance $a_0 = 10$ Å.

In the calculations above it was assumed that the lattice parameter is the same for bulk, surface and on the substrate. A small change in the lattice parameter has a large effect on the polarization energy. The induced dipole moment on a site is proportional to the square of the distance between this site and the charges. The energy stored in the dipole is again proportional to the square of the dipole moment, so that in the end the polarization energy is proportional to the distance to the power four. In figure 2.4 the total polarization energy is plotted as a function of the lattice contraction/expansion. It is found that $\frac{\partial 2E_p}{\partial a} \mid_{a_0} = 0.43$ eV/Å, i.e. in bulk C_{60} a lattice contraction of 10% leads to a substantial reduction of the effective U of about 0.4 eV.

C_{60} can be intercalated with for instance alkali atoms. The charge transfer from the alkali atoms to the bucky-balls is nearly complete and an ionic alkali-C_{60} lattice is formed. The alkali ions are small and find a place in empty spaces between the fullerenes. In calculating the polarization energy in this ionic lattice, the ionic polarizability of the alkali ions can be neglected and the molecular polarizability of charged C_{60} has to be used. Their theoretical values can be found in reference [22]. Due to Jahn-Teller distortions on the bucky-ball the on-site Coulomb interaction in a C_{60}^{n-} ion is different from U^{at} for the neutral molecule [23, 24]. In the table below the change U due to the Jahn-Teller distortions is denoted by U^{JT}. The effective Coulomb interaction is then calculated assuming that the C_{60}-C_{60} distance is constant. The polarization screening combined with the Jahn-Teller distortion lead to significant variations in the effective Coulomb interaction.

Effective Coulomb interaction for C_{60}^{n-}				
n	α	$2Ep$	U^{JT}	U^{eff}
0	89.8	1.65	-	1.75
1	163.7	2.20	-0.2	1.00
2	157.4	2.16	0.4	1.64
3	129.4	1.97	-0.2	1.23
4	138.6	2.03	0.4	1.77
5	157.3	2.16	-0.2	1.04
6	150.9	2.12	-	-

Longer range Coulomb interactions are found to be well described by a $1/\epsilon R$ behavior. In the light of the following chapter the question may be raised why a charge density wave type of charge ordering is not observed in experiments on bulk C_{60}. If only the on-site and nearest neighbor Coulomb interaction are considered, it is energetically favorable for electrons to avoid nearest-neighbor Coulomb interactions and to form a super-lattice of positive and negative charged ions, especially since the coordination number in a FCC lattice, 12, is very high. There are some considerations that weaken and some that strengthen this line of argument. First, if the charge density wave (CDW) doesn't break the inversion symmetry of the electron density, polarization screening does not contribute to the energy in the charge ordered state, in analogy to the Madelung potential that is unscreened. As polarization screening also does not contribute to the ground-state energy, the *bare* Coulomb interactions determine the phase transition. The ratio V^{bare}/U^{bare} is even larger than V^{eff}/U^{eff} for bulk C_{60}, so one would have even more reason to expect a CDW ordering. Also the possibility for a non inversion-symmetric charge distribution, that is favored by the polarization energy, is left open. Second, in a FCC lattice the formation of a simple CDW is not favorable because of the frustration of this type of charge ordering. It does, however, allow for more complicated forms of charge density waves. Third, a finite bandwidth W might destroy a static charge density wave. In C_{60},however, W is about 0.5 eV [25], much smaller than U^{eff} and comparable to V^{eff} so that one expects CDW correlations to survive. Third, the HOMO-LUMO splitting Δ in C_{60} is about 1.6 eV. The orbital energy splitting acts against any form of charge disproportionation. Finally longer range Coulomb interactions oppose the formation of a CDW. As the *bare* longer range Coulomb interactions are not small they can prevent the formation of a charge density wave.

It is, in conclusion, an open question why C_{60} does not display features of charge density ordering. More quantitative analysis is needed to give a decisive answer to this question.

Results for 3D systems

The polarization energy is calculated exactly for a model system where the lattice spacing is taken to be unity. In figure 2.5 the result is shown for $\alpha = 0.05$ and $\alpha = 0.1$, corresponding with $\epsilon = 1.79$ and $\epsilon = 3.16$ respectively. The figure shows

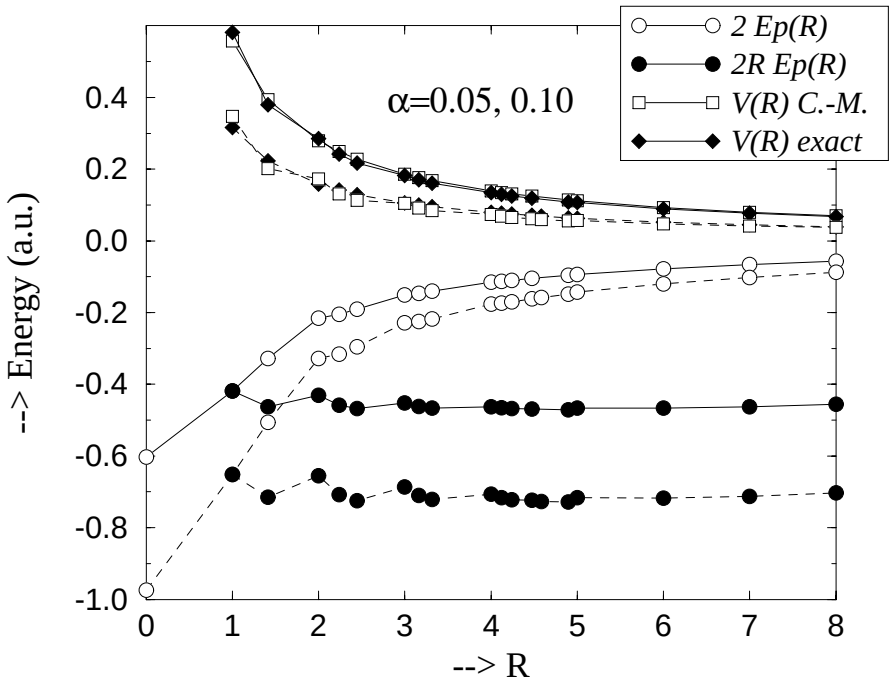

Figure 2.5: The polarization energy $2E_p$ as a function of separation between the electrons for a three dimensional system. The lattice spacing is taken to be unity. The full lines are for $\alpha = 0.05$, the dashed ones for $\alpha = 0.1$

that the polarization energy is proportional to 1/R at large separations between the charges. At short distances the exact potential fluctuates slightly around the C.-M. result. The deviations are not larger than 10%. At larger distances the two potentials coincide.

Low-dimensional systems

Consider a system where the dipoles and electrons are confined to a plane (2D system) or a line (1D system). This system is placed in the 3D space, so the $1/|R|$ Coulomb interaction between the two electrons has to be used. When the continuum integral (2.9) is evaluated in these two low dimensional cases, we see that the outcome does not only depended on the distance between the two electrons, but also on the range of integration. In order to make the integral convergent we have to assume a sphere around each electron with radius r_0, in which the polarizability is zero. The result of the integration depends on the unknown quantity r_0, an artifact that arises because of the continuum limit. This is illustrated in figure 2.6, where the outcome of continuum integral as a function of separation between the electrons is plotted. For clarity the proportionality constants are set to unity. The behavior for the 3D system is as expected: the polarization energy is negative and proportional to $1/|R|$. In the 1D system, however, the polarization energy is positive, implying that screening effects

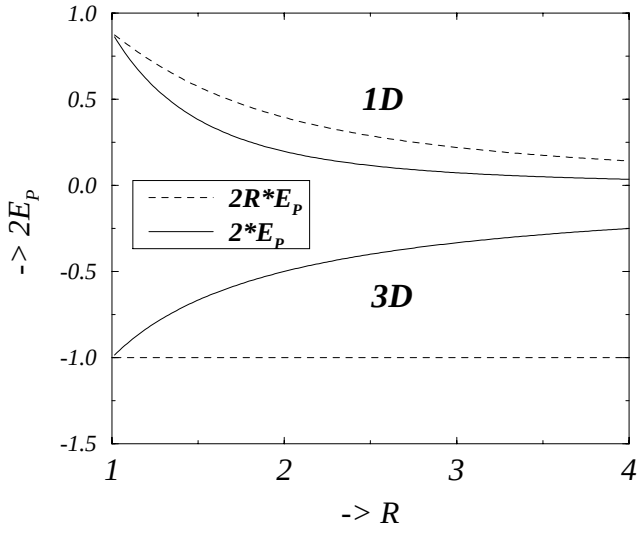

Figure 2.6: The polarization energy $2E_p$ as a function of separation between the electrons in one and three dimensions in the continuum limit. The lattice spacing is taken to be unity and in the 1D system $r_0 = 0.5$.

increase the repulsion between the charges. Moreover at short distances the integral is found to diverge when $r_0 \to 0$ and at large distances the polarization energy decays faster than $1/|R|$.

That the polarization energy falls of faster than $1/|R|$ at large distances can be expected since in 1 and 2D the integration is not over a volume, but rather over a line and a surface respectively. The consequence of this is that at large distances in low dimensional systems one cannot define a dielectric constant anymore and that in systems where the dimensionality of the Coulomb interaction is larger than the dimensionality of the system, the Coulomb potential is unscreened at large distances [26]. At small distances the screening is fully due to local field effects.

That this also is the case when the polarization energy is calculated exactly, is illustrated in Fig. 2.7, where the polarization energy $\mathrm{E_p}$ for a one dimensional line of atoms in a three dimensional space is evaluated. This geometry can be encountered in a material where a chain of polarizable atoms is embedded in a matrix of non polarizing atoms. At very short distances (till about 2 lattice spacings) the Coulomb interaction is screened. So the exact calculation shows that the divergency at short distances found in the continuum limit is an artifact of this limit. However, when the separation between the charges is larger, the Coulomb interaction is *anti-screened*: the induced polarization results in an increased repulsion between the two charges. In the figure also RE_p as a function of distance is shown. If a dielectric constant ϵ can be defined then $2RE_p = 1 - 1/\epsilon$. From the figure it can be seen that $2RE_p \to 0$ when $R \to \infty$, so that at large distances $\epsilon \to 1$ and the Coulomb potential is unscreened. The consequence of this is that the effective potential between the charges is flattened out: at short distances the bare Coulomb potential is large, but also the polarization energy is large, see figure 2.8. At intermediate distances the Coulomb potential

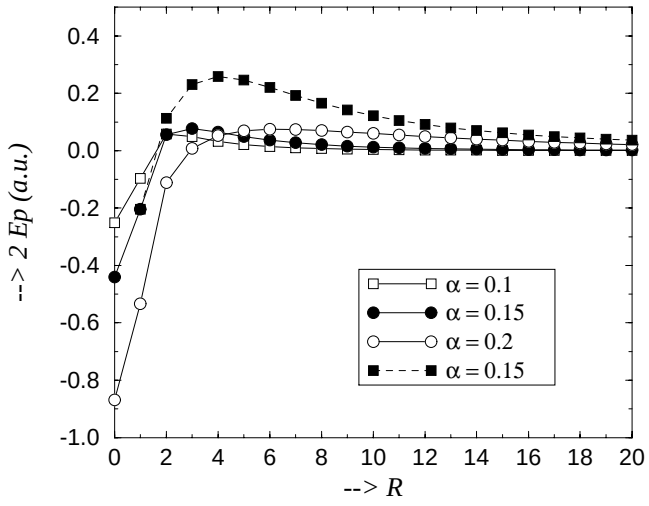

Figure 2.7: The polarization energy $2E_p$ as a function of separation between the electrons in one dimension. The lattice spacing is taken to be unity. The dashed line represents $2RE_p$ for $\alpha = 0.15$

decays, but the polarization enhances the repulsive interaction so that in the end the effective potential decays much slower than 1/R.

In a two dimensional system an analogue situation is encountered. At short distances local fields screen the potential and at large distances the potential is again unscreened, see Fig. 2.9. Qualitatively the occurrence of anti-screening in 1D and the lack thereof in 2D can be understood by realizing that the screening of the Coulomb potential is due to the interaction of the induced polarization cloud of charge A with the cloud of charge B. The induced dipole moment is proportional to the electric field squared at a lattice site and if dipole-dipole interactions are neglected, the sum of the electric fields of charge A and B determines the total field at a site. There is a region where the two fields amplify each other, and a region where the two fields counteract. In figure 2.10 the region where the two fields counteract is shown: it lies inside the square in the middle of the figure. Outside this region the angle between the two field vectors is smaller than $\pi/2$ and the resultant field is larger than either the field of A or the field of B alone.

In a one dimensional system the region where the two fields counteract consists of all atoms between the two charges. If the separation between the charges is small, this region is small and the largest contribution to the polarization energy comes from the region where the two fields amplify each other, resulting in a negative polarization energy. When the distance between the charges grows, however, two effects are present. First, the region where the fields counteract becomes larger and second, the electric fields in the region where the fields amplify, get smaller. This results in a positive polarization energy and anti-screening. In two dimensions the region where the fields amplify each other is relatively much bigger than the region where the two fields counteract compared to the 1D case. Due to this, the counteracting fields never

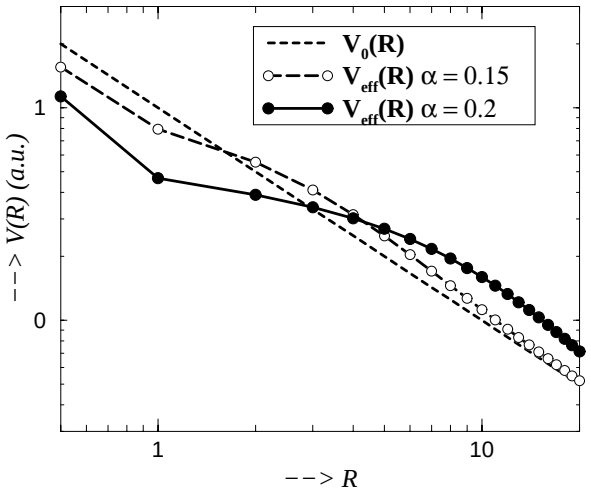

Figure 2.8: Effective Coulomb potential in a 1D system for U=2.0, $\alpha = 0$, $\alpha = 0.15$ and $\alpha = 0.2$ on a Log-Log scale. The dashed straight line represents the unscreened Coulomb interaction. Screening tends to flatten the effective potential at intermediate distances. The lattice spacing is taken to be unity.

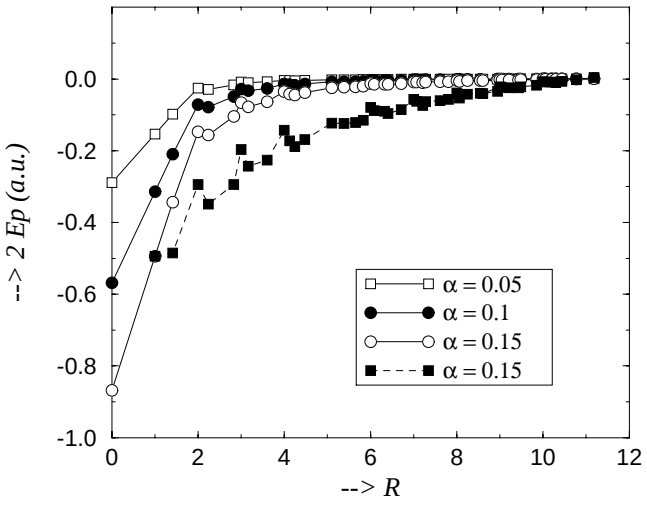

Figure 2.9: The polarization energy $2E_p$ as a function of separation between the electrons for a two dimensional cubic lattice. The lattice spacing is taken to be unity. The dashed line represents $2RE_p$ for $\alpha = 0.15$

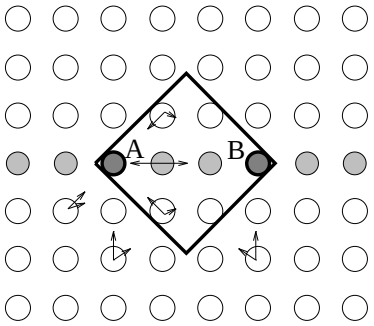

Figure 2.10: Schematic representation of the polarization effects in one and two dimensions. The arrows represent the electric fields of charge A and B (not on scale). Inside the square in the center of the figure the electric fields of charge A and B counteract, outside the square the two fields reenforce each-other

give a contribution to the polarization energy that is larger than the contribution of the amplifying fields.

2.3 Conclusions

We can sum up the findings of this chapter up in a few conclusions. First, it was argued that screening of the Coulomb repulsion in non-polar insulators can be calculated using a point-dipole model. Within the partial continuum limit of this model, where dipole-dipole interactions are taken into account on the Clausius-Mossotti level, values for the polarization energy and the effective on-site Coulomb interaction U that compare well with experiment can be obtained. It was shown that the Madelung potential and also atomic multipole Coulomb interactions are unscreened.

Applying the formalism to C_{60}, effective values for the bulk Coulomb interaction are obtained that agree well with experiment. The effective U for C_{60} on the surface, on metallic substrates and in compounds with ionic C_{60} was calculated. Metallic substrates are found to screen U and the nearest neighbor Coulomb interaction V very efficiently. Furthermore it was shown that small lattice contractions can cause a substantial reduction of U.

Finally, for three dimensional systems the deviations from the Clausius-Mossotti result for the off-site screened Coulomb interaction are found to be small. In one and two dimensional systems, however, only local field effects contribute to the screening. At large distances the Coulomb interaction is unscreened and in 1D at intermediate distances the Coulomb interaction is even anti-screened.

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